

**Welsh  
Composites  
Centre**



# **Thermal Analysis Methods for Composites**

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# Welsh Composites Centre

- A “Knowledge Transfer Centre”, based in Swansea University
- To provide technical support in composites technology to SME’s across Wales
- Linking in with composites expertise across Wales and beyond
- Activities include seminars, webinars, collaborative R&D
- [www.welshcomposites.co.uk](http://www.welshcomposites.co.uk)



# What do we mean by thermal analysis?

## Thermal behaviour

- Thermoset curing characteristics
- Glass transition and melting temperatures
- Thermal conductivity and expansion
- Heat capacity

## Structure and composition

- Material composition
- Crystallinity
- Molecular orientation

## Mechanical behaviour

- Viscoelastic properties
- Fibre and interface strength

## Degradation

- Thermal weight loss
- Oxidative stability

# Structure of webinar

We will talk through these in terms of the equipment used for the analysis:

- Differential scanning calorimetry
- Thermal gravimetric analysis
- Dynamic mechanical thermal analysis
- Thermal conductivity measurement

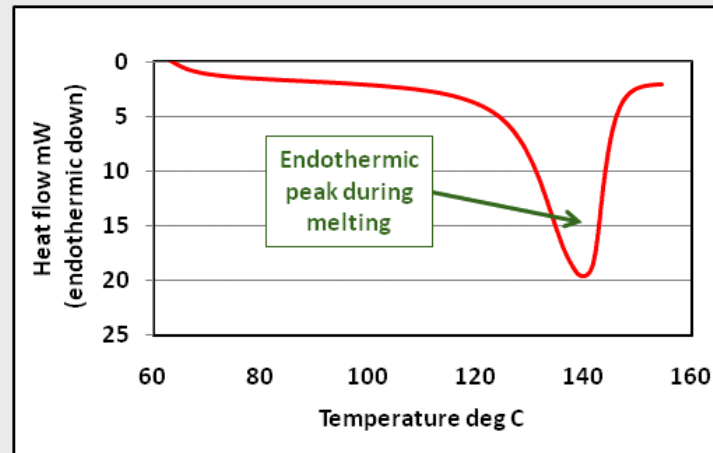
.... and stop for questions after each section.

# Equipment – Differential Scanning Calorimeter (DSC)

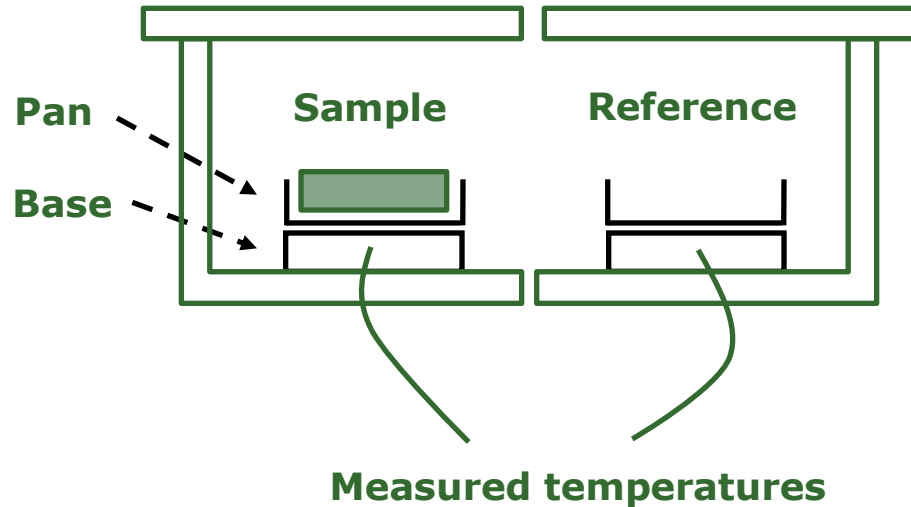
Allows analysis of properties and processes that can be characterised by heat flow in or out of a sample, e.g.

- Curing of thermosets
- Phase transitions
- Oxidation

e.g. The melting point of a polymer can be used to identify the polymer

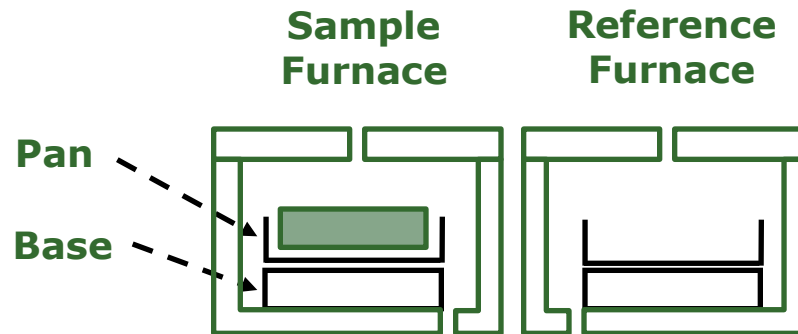


# Heat Flux DSC – Single Furnace



- Furnace controlled to programmed temperature profile
- Measures temperature difference between sample and reference
- Calculates corresponding heat flow in to or out of sample from calibration data

# Power Controlled DSC – Double Furnace



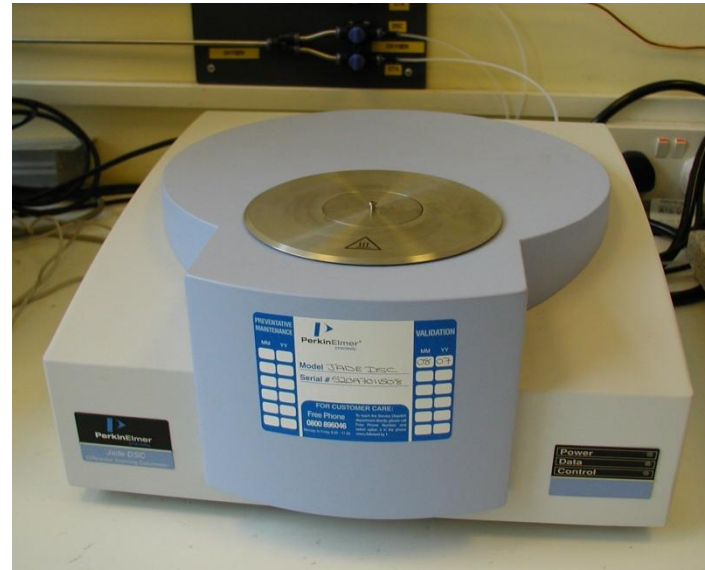
- Both furnaces controlled to programmed temperature profile
- Measures difference in energy input/output required to achieve temperature
- Faster heating and cooling rates
- Better resolution and sensitivity

# DSC options

Other DSC options:

- **Modulated Temperature DSC**  
Applies a non-linear heating or cooling rate, typically a sinusoidal signal, to allow separation of in-phase and out-of-phase phenomena e.g.  $T_g$  and decomposition.
- **Hyper DSC (on power controlled DSC)**  
Applies very fast heating rates to increase sensitivity or identify kinetic behaviour
- **Hyphenated techniques**  
The connection of a DSC to another analysis technique such as MS, IR, FT-IR, Raman
- **UV-DSC**  
Exposure of the sample to UV light during a run e.g. to study UV curing
- **HP-DSC**  
Uses a high pressure furnace

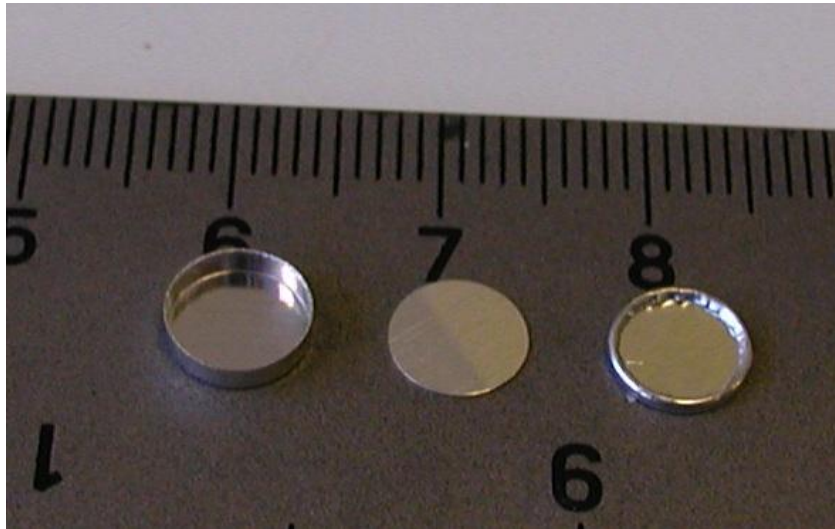
# Perkin Elmer Jade DSC



- Heat flux DSC
- Temperatures from 15°C to 450°C
- Heating rate to 100°C / min
- Switchable nitrogen or oxygen purge gas

# Perkin Elmer Jade DSC

Sample pans and samples



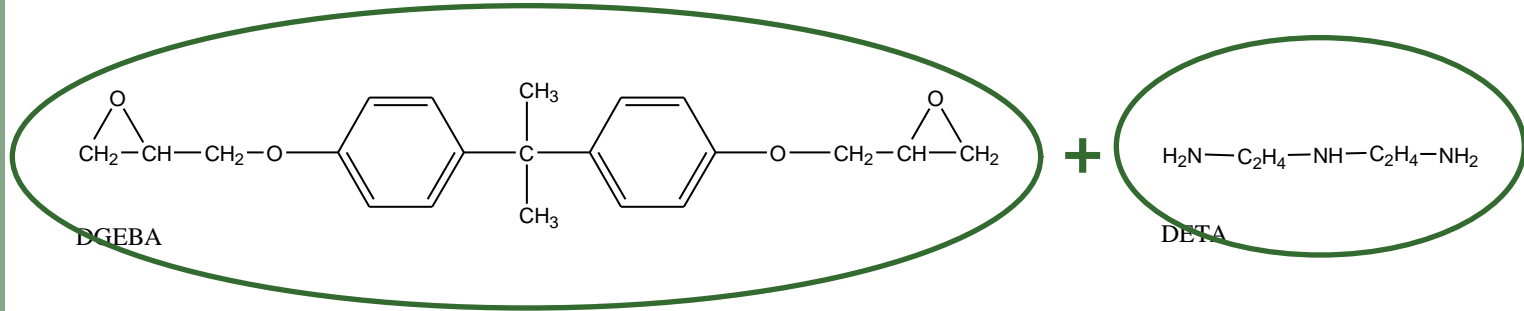
# Perkin Elmer Jade DSC



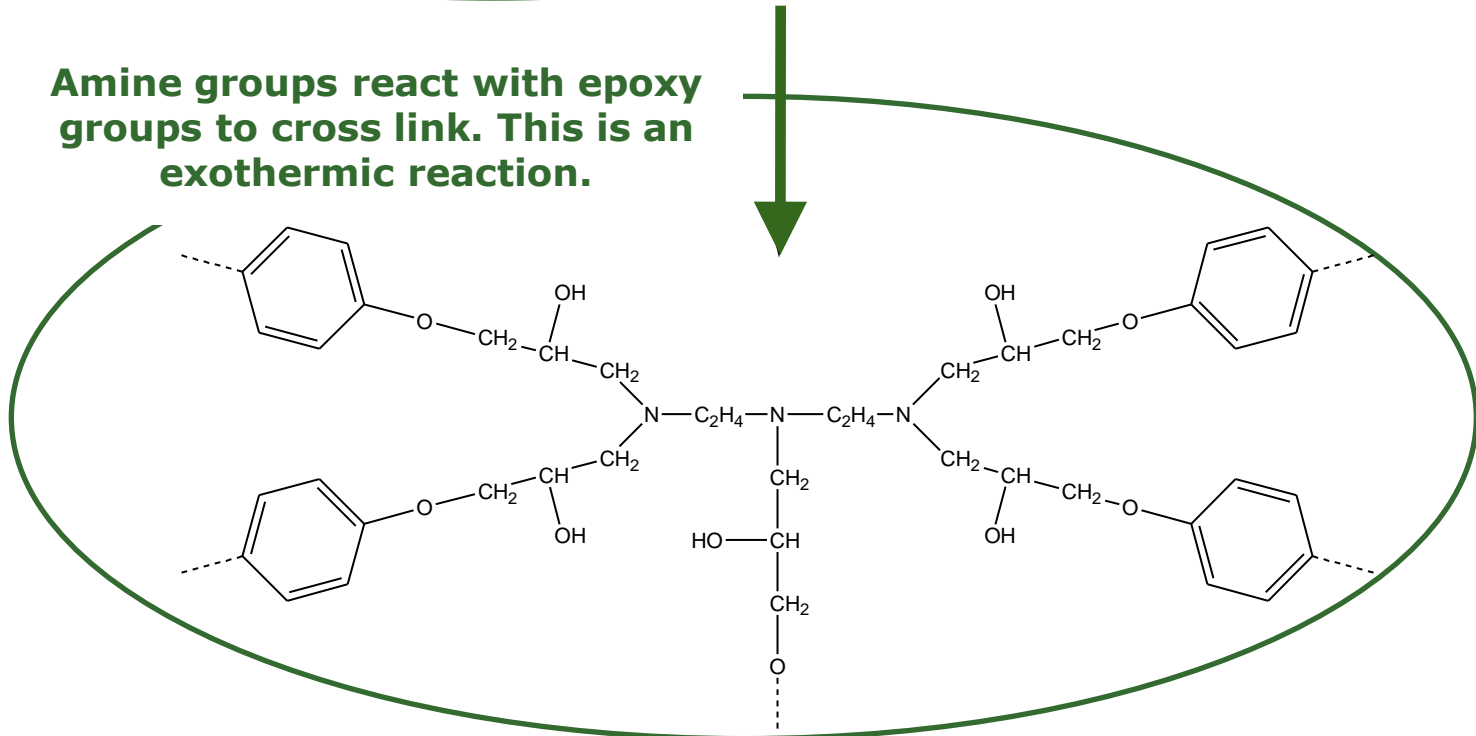
# Thermoset curing characteristics

**Epoxy resin**  
(diglycidyl ether of bisphenol-A)

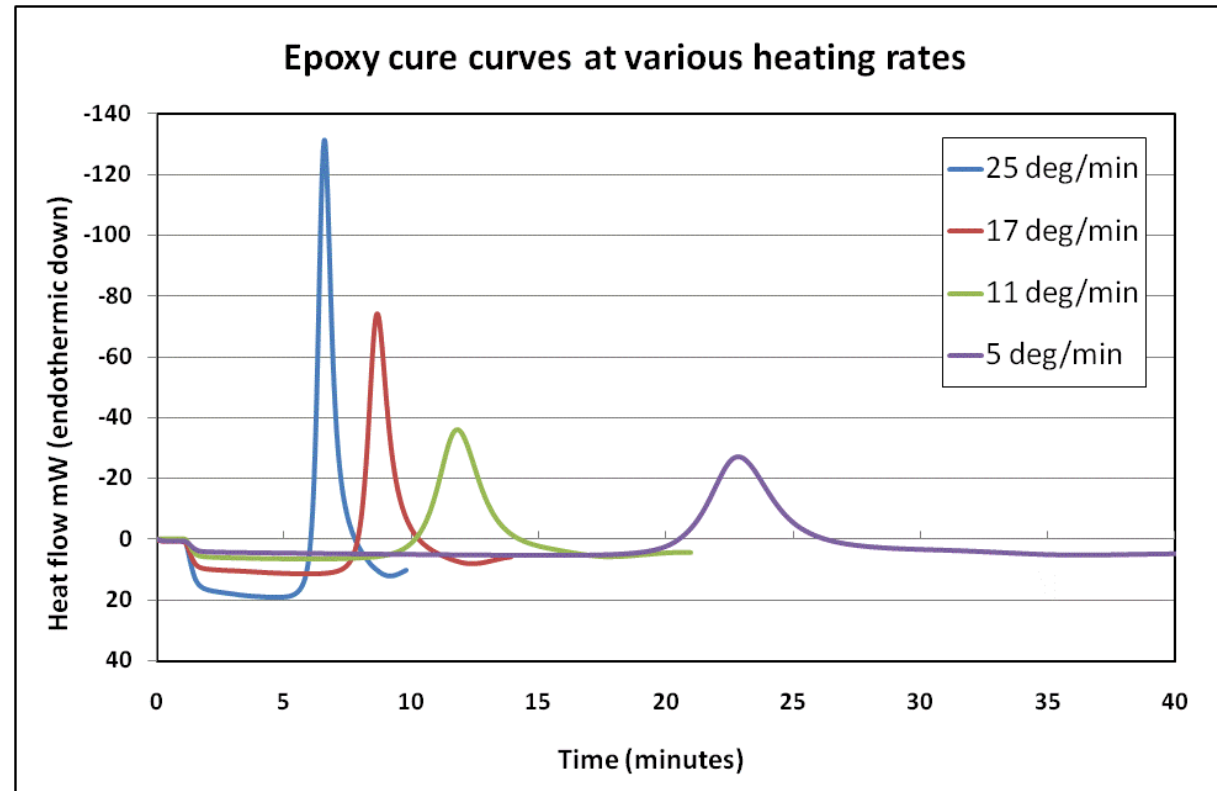
**Hardener**  
(diethylenetriamine)



**Amine groups react with epoxy groups to cross link. This is an exothermic reaction.**



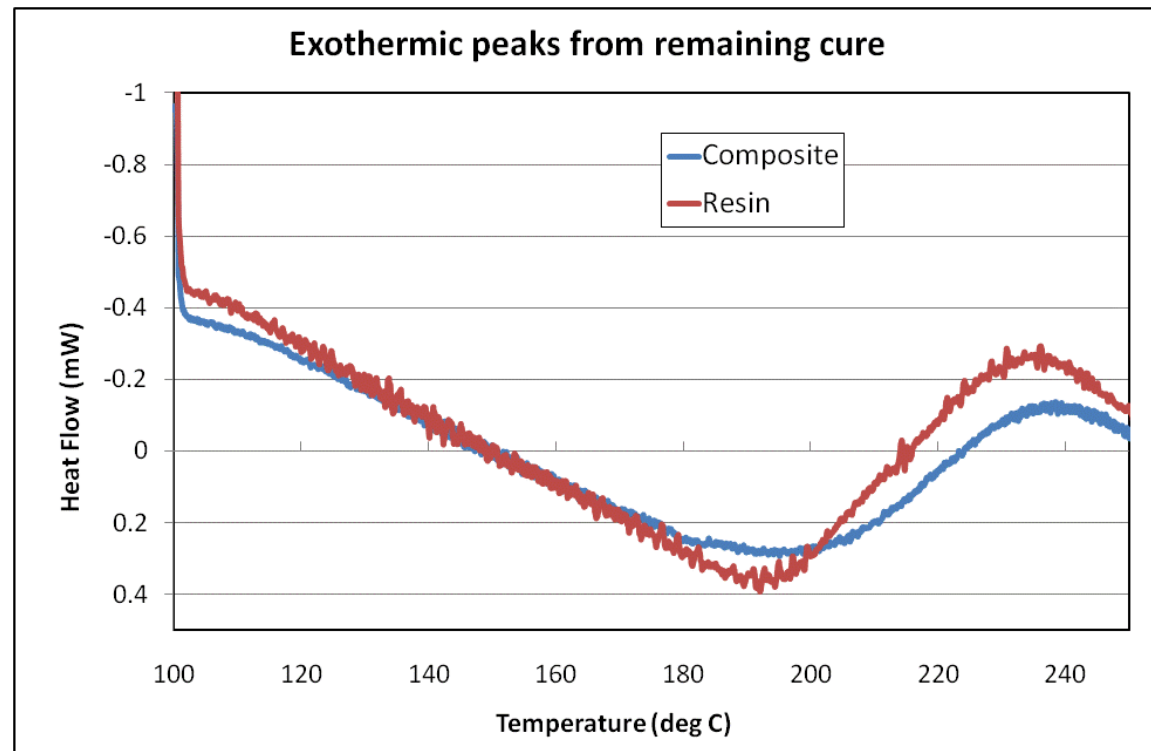
# Curing of Thermosets



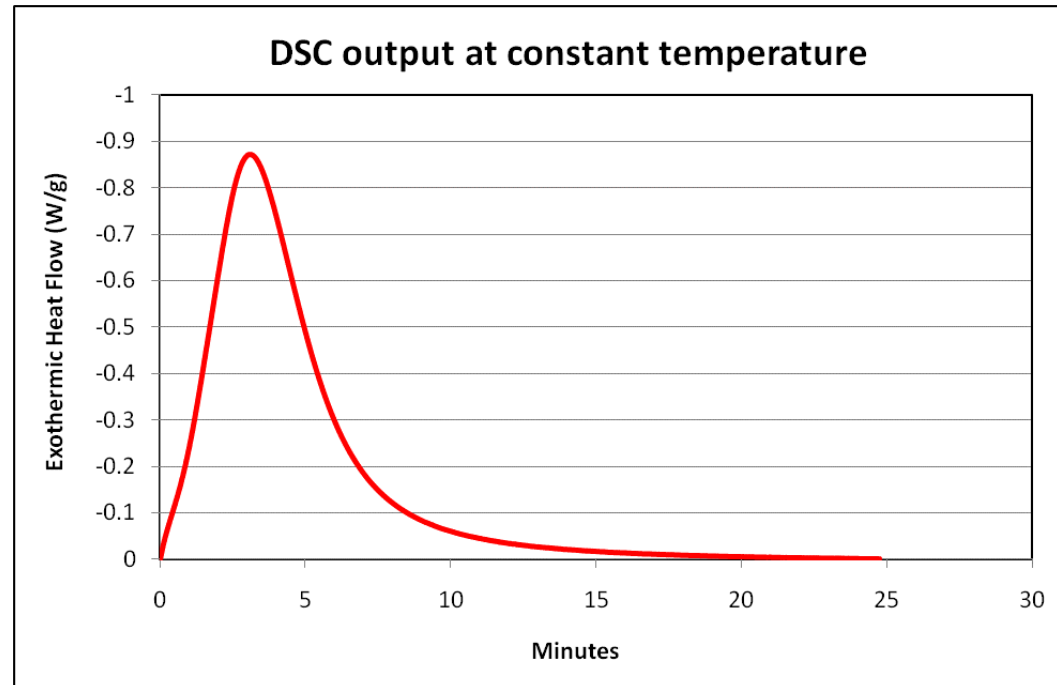
- First step is to establish the average “heat of cure”
- Curing is carried out at a number of different heating rates
- “Heat of cure” is the area under the DSC curve

# Curing of Thermosets

- This can be used to establish the amount of cure of a sample
- If it is not fully cured, there will be an exothermic peak during heating
- The area of this peak as a proportion of the total heat of cure is the “uncured” percentage

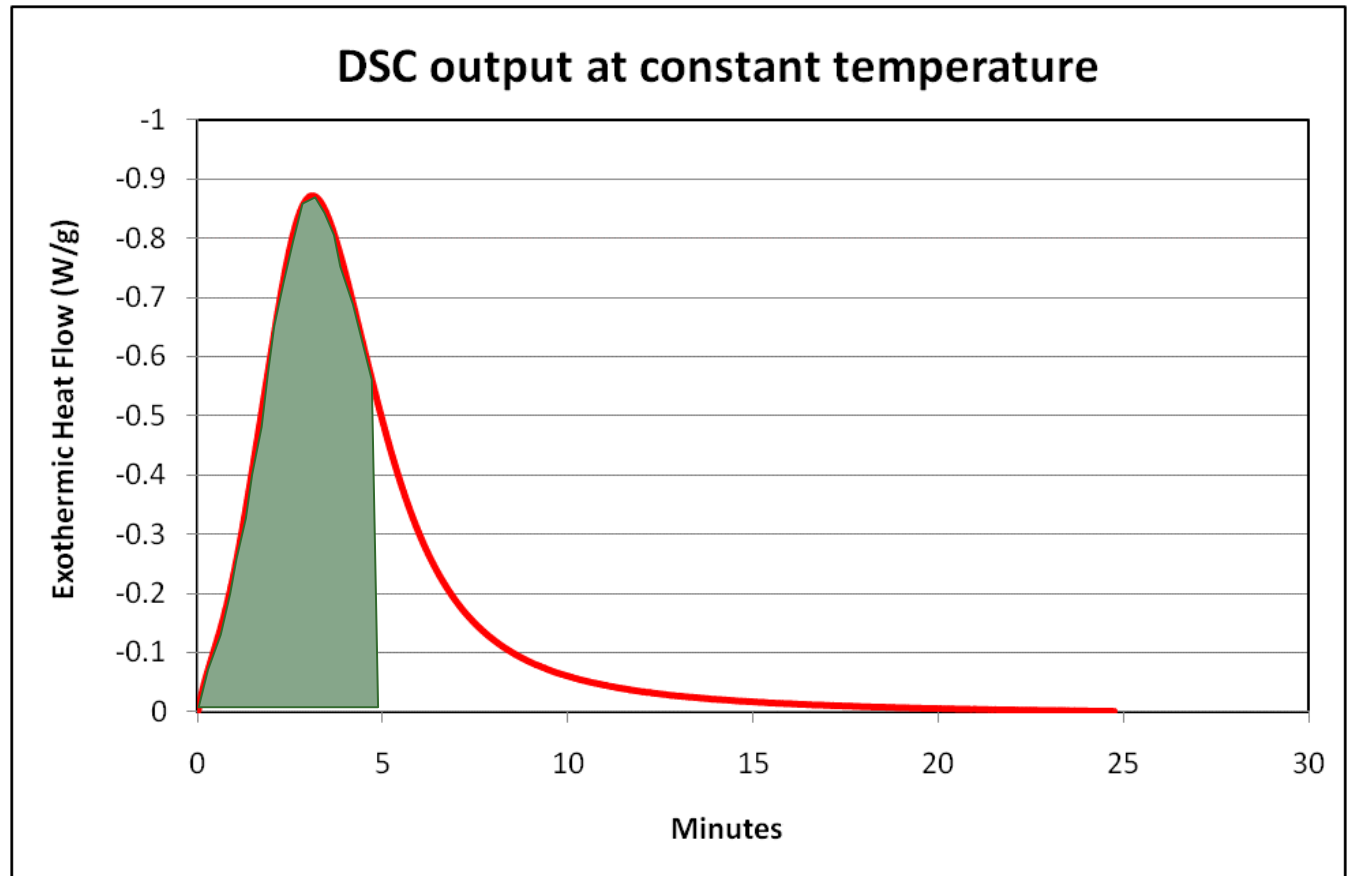


# Thermoset curing kinetics



- To obtain kinetic parameters, a number of isothermal runs are carried out at different temperatures.
- Epoxy curing is an autocatalytic reaction so heat output starts very small then builds up. Need a power controlled DSC to achieve high accuracy for the initial reaction.

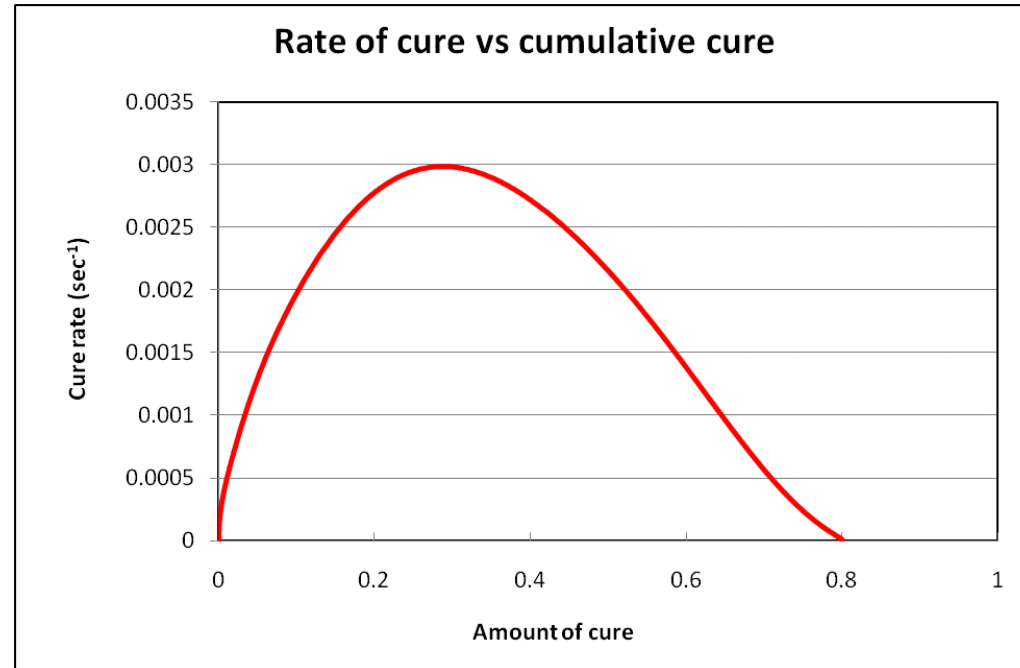
# Thermoset curing characteristics



At any given time on the heat flow curve,

- Cure rate = heat flow / total heat of cure
- Amount of cure = area under curve / total heat of cure

# Thermoset curing characteristics



This gives us a graph of rate of cure vs amount of cure for each temperature.

These curves can be fitted to a typical cure equation

e.g.

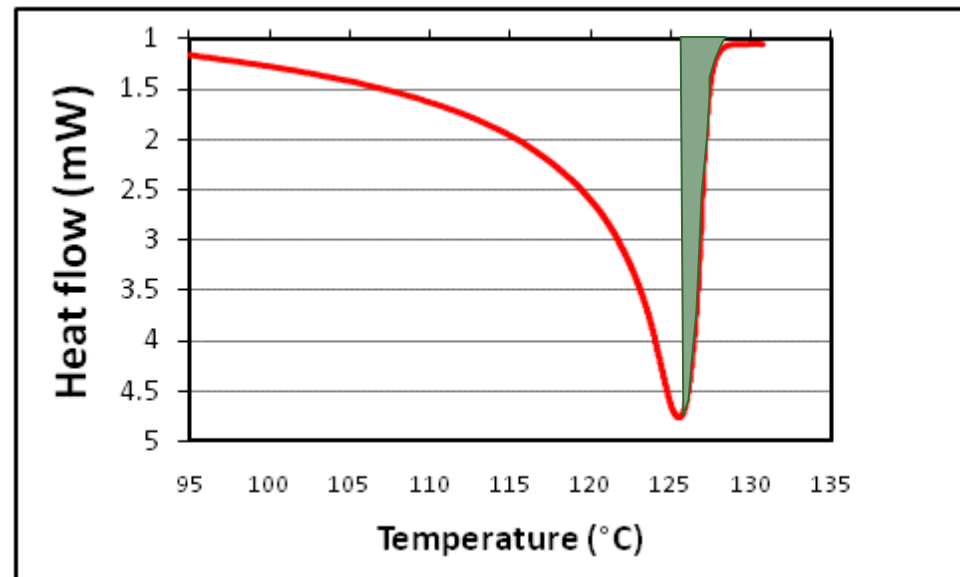
$$\frac{d\alpha}{dt} = (k_1 + k_2 \cdot \alpha^m) \cdot (\alpha_{max} - \alpha)^n$$

where

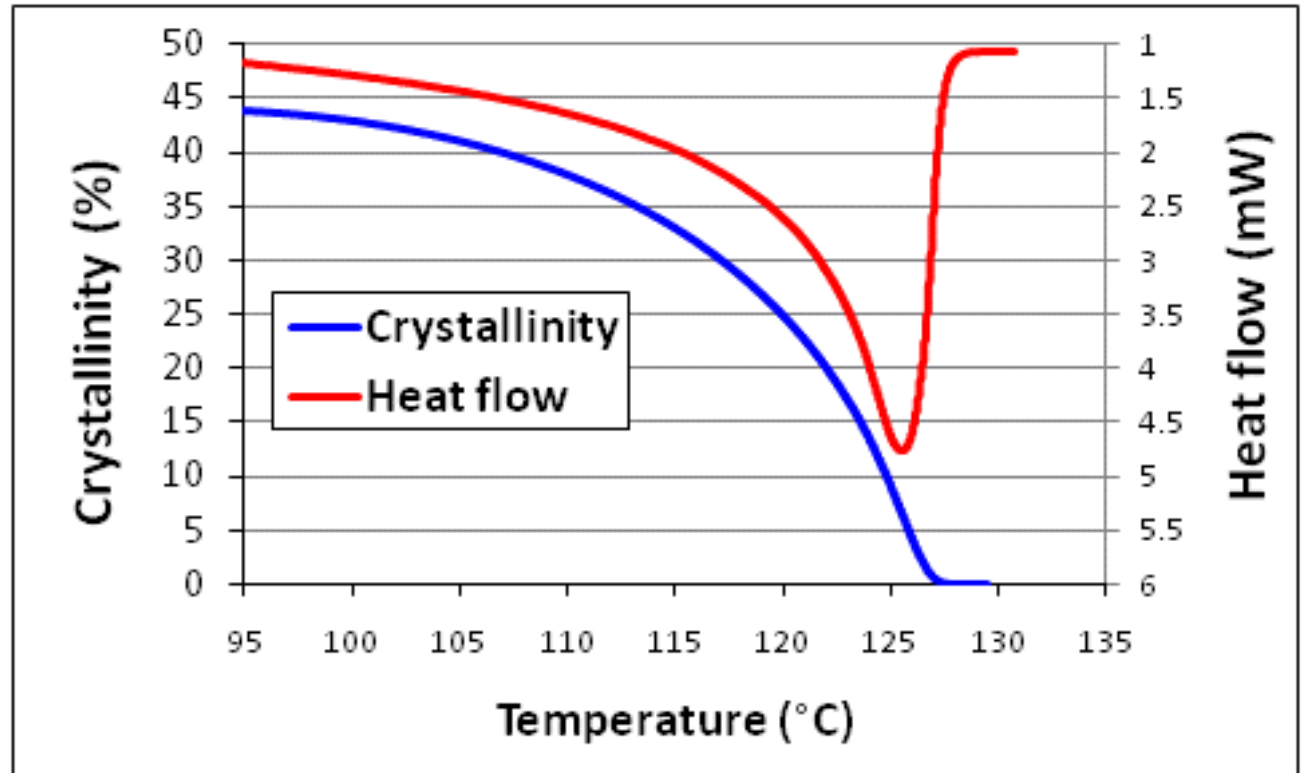
$$k_i = A_i \cdot e^{-E_i/(RT)}$$

# Crystal structure

- For semi-crystalline polymers, e.g. Nylon, PP, PEEK, the degree of crystallinity can be calculated from the heat of melting.
- The total heat needed to melt a 100% crystalline material,  $H_t$ , is available from reference data.
- Assuming zero crystallinity above the melting point, at each lower temperature the cumulative area under the curve, as a proportion of  $H_t$ , gives the % crystallinity.



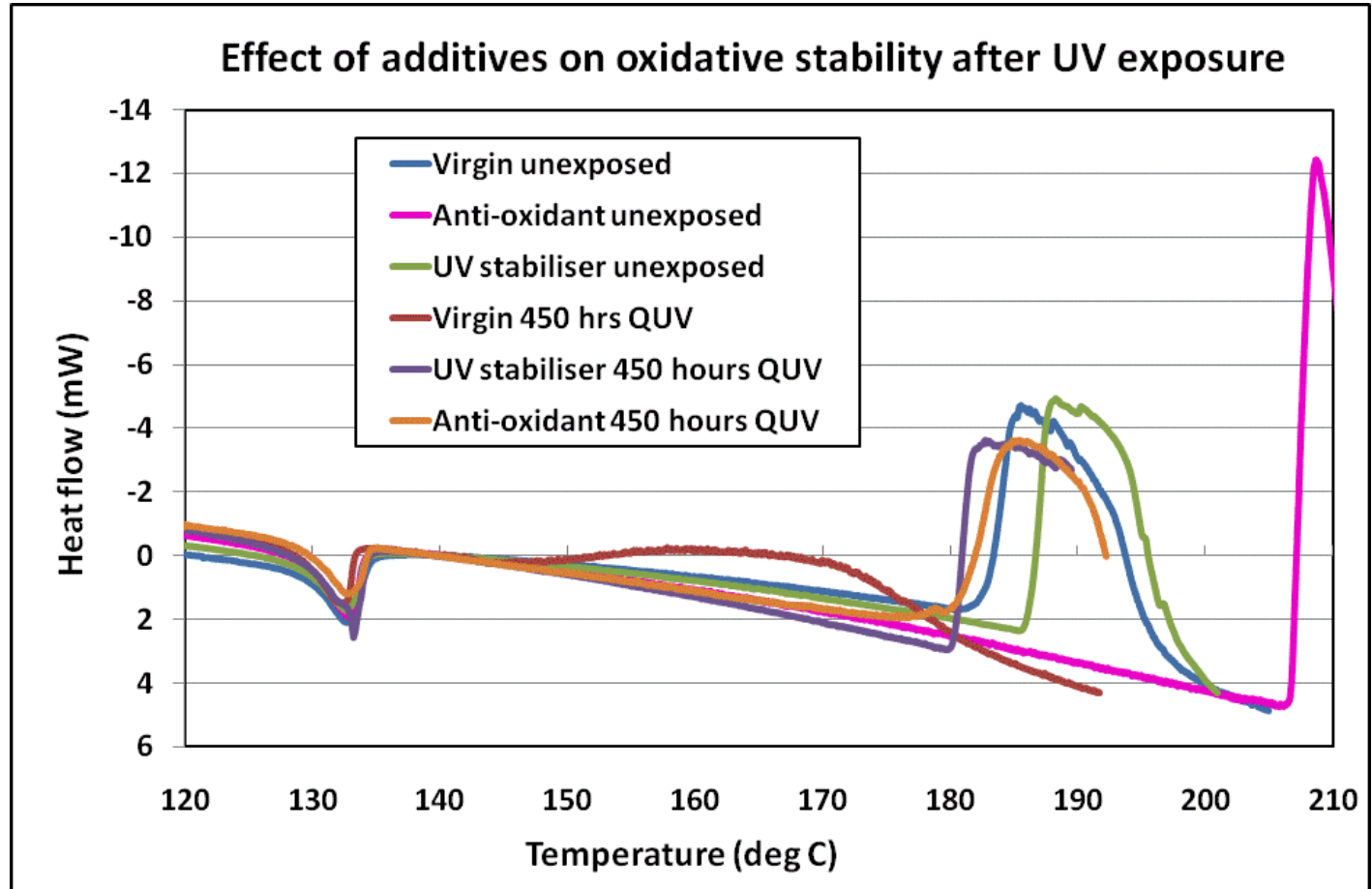
# Crystal structure



# Oxidative stability

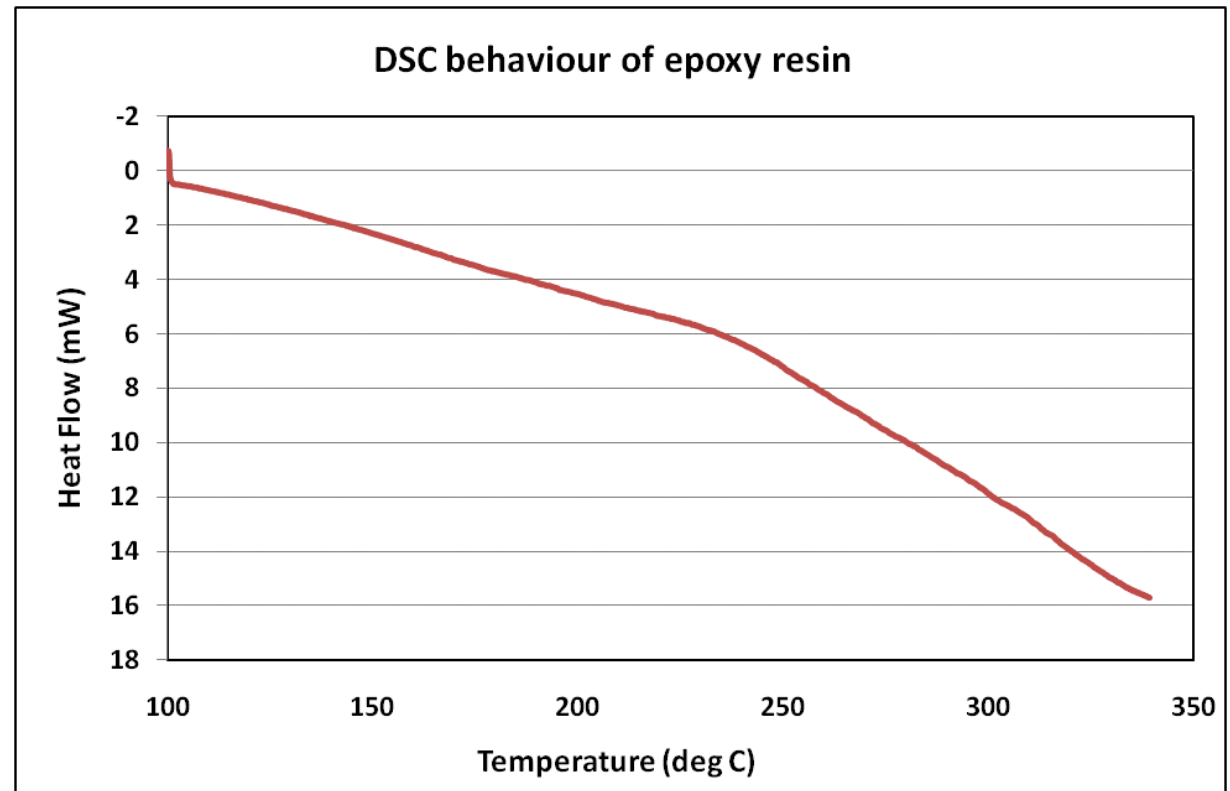
- Oxidation is an exothermic reaction so can be detected by a DSC
- Two measures are used:
  - Oxidative induction time (OIT) – the time to the start of the oxidation exotherm during an isothermal run
  - Oxidative induction temperature (OItemp) – the temperature at which the oxidation exotherm starts during a temperature ramp
- The OIT or OItemp will decrease as the oxidative stability of the sample decreases, e.g. due to loss of stabiliser or increased degradation

# Oxidative stability



# Limitations of OIT/OItemp

- Good for thermoplastics, especially polyolefins
- Not so easy with thermosets
- E.g. epoxy (below) shows no clear oxidation peak
- Will not pick up non-oxidative degradation

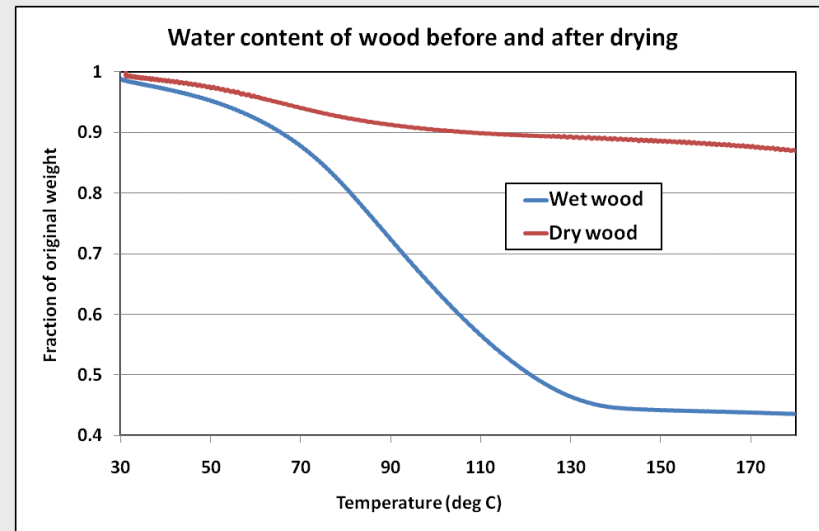


# Equipment – Thermal Gravimetric Analyser

Sensitive balance measures weight loss from a sample as it goes through a programmed temperature cycle.

Used to determine  
e.g.

- Moisture content
- Material composition
- Thermal stability and degradation
- Fibre content



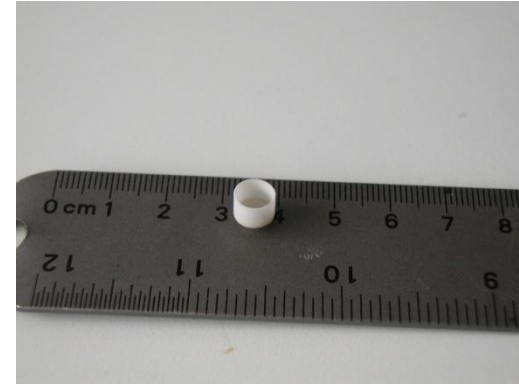
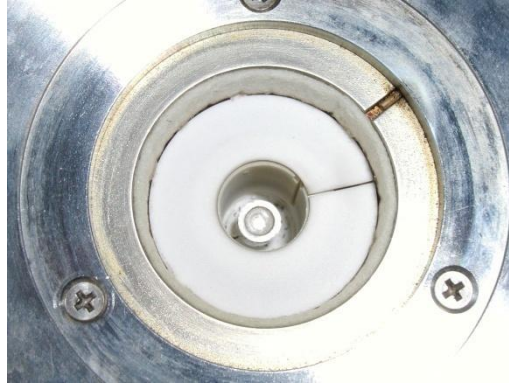
Could link to further analysis equipment e.g. MS, FTIR.

## Perkin Elmer STA6000



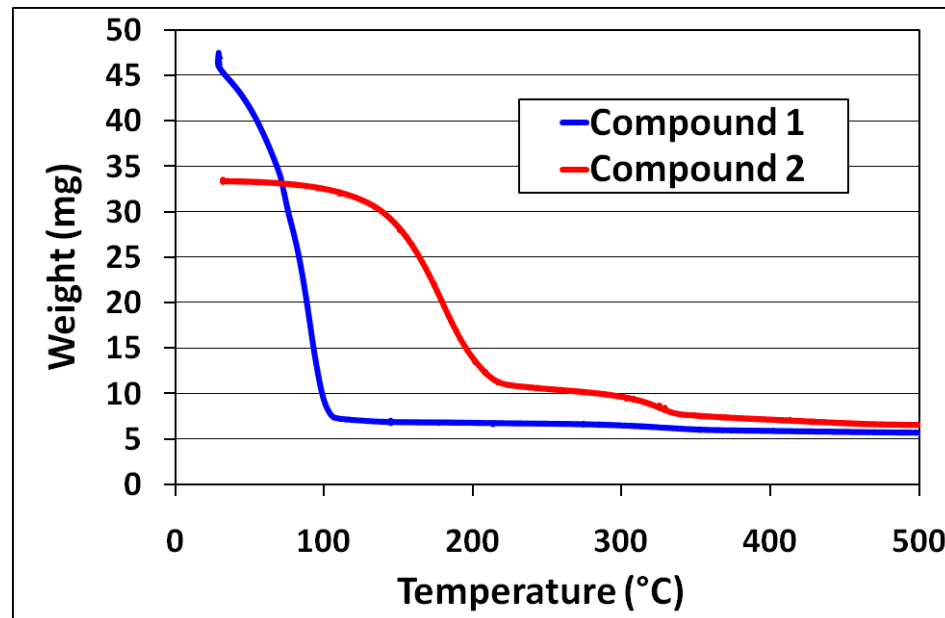
STA – Simultaneous thermal analyser  
Includes heat flow measurement but not as accurate as DSC  
Temperatures from 15°C to 950°C  
Switchable nitrogen or oxygen purge gas

# Perkin Elmer STA6000



# Material composition

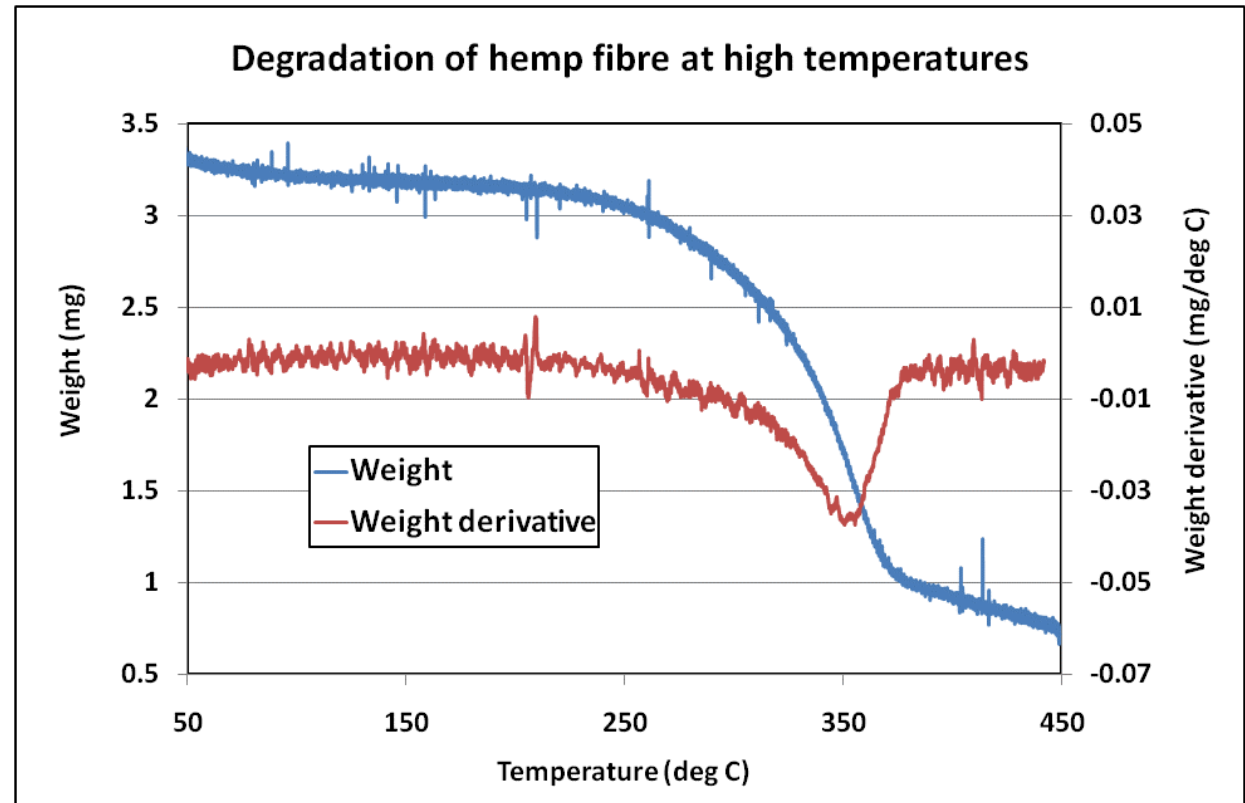
- Compounds 1 and 2 were a mixture of organic and inorganic components.
- Different components will be driven off at different temperatures.
- Traces indicate that Compound 1 contained a single organic component driven off between 30°C and 100°C whilst Compound 2 contained two components driven off at around 170°C and 310°C.



# Thermal stability of fibres

e.g. Study of natural fibres to establish safe processing temperatures

- Hemp fibre starts to degrade at about 220°C – initially hemi-cellulose or pectin
- Faster degradation from around 300°C - cellulose



# Equipment – Dynamic Mechanical Thermal Analysis (DMTA)

Performs small mechanical deformations while controlling temperature

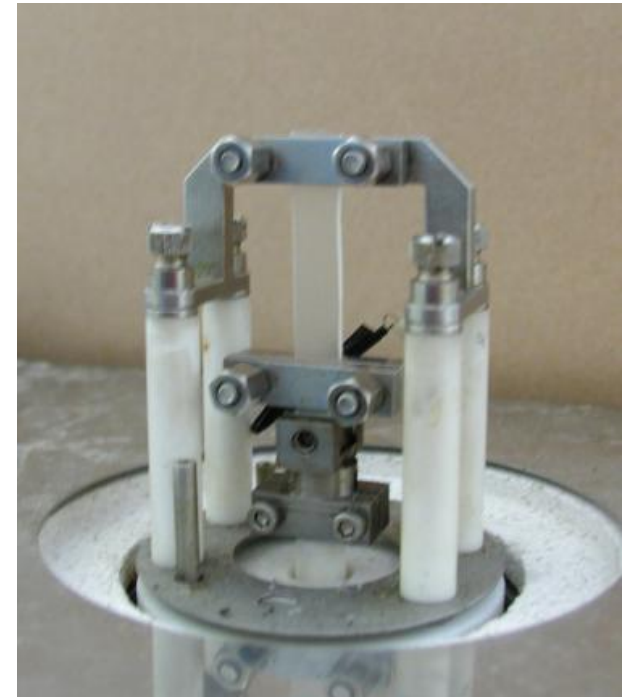
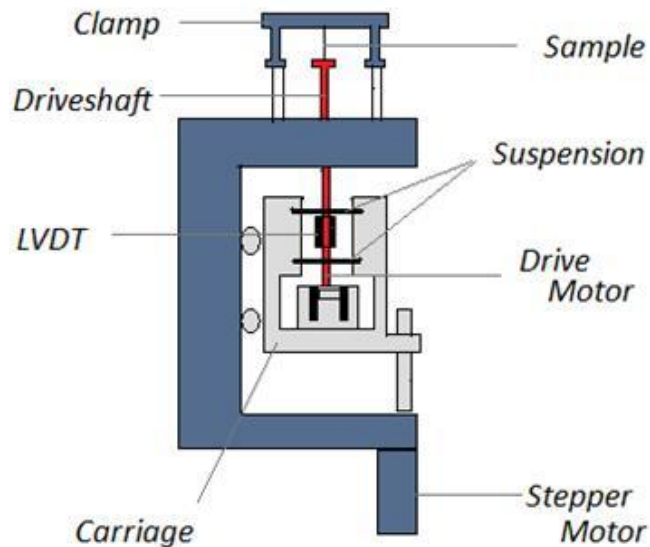
Used to determine

- Viscoelastic behaviour
- Glass transition temperature
- Interfacial bond strength
- Thermal expansion



# DMTA Basics

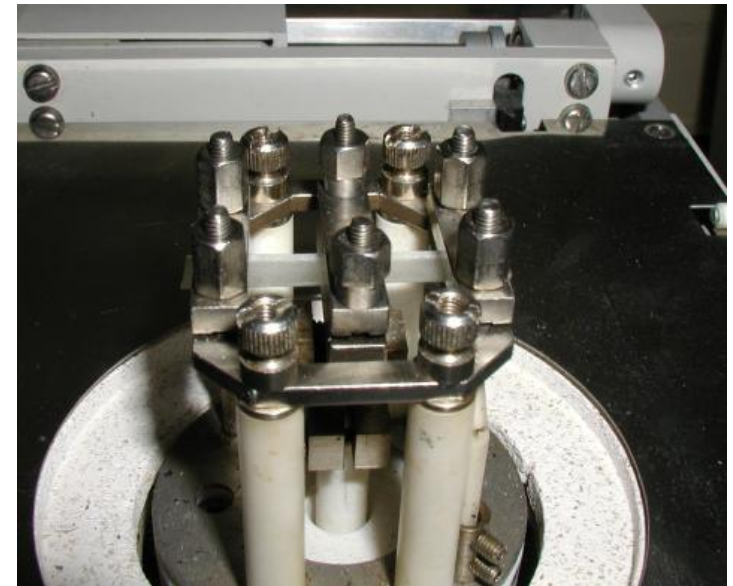
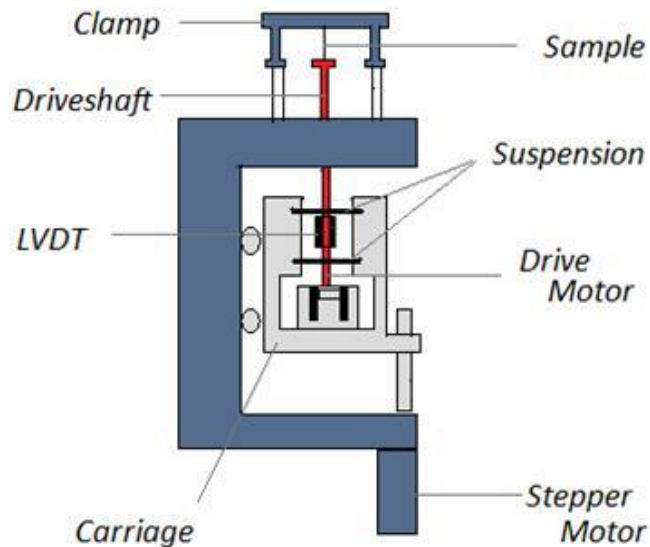
- Small sample held in clamps of various geometries
- Controlled dynamic displacement applied
- Dynamic force measured
- Temperature controlled, typically over range from -100°to +300°C.



Tension

# DMTA Basics

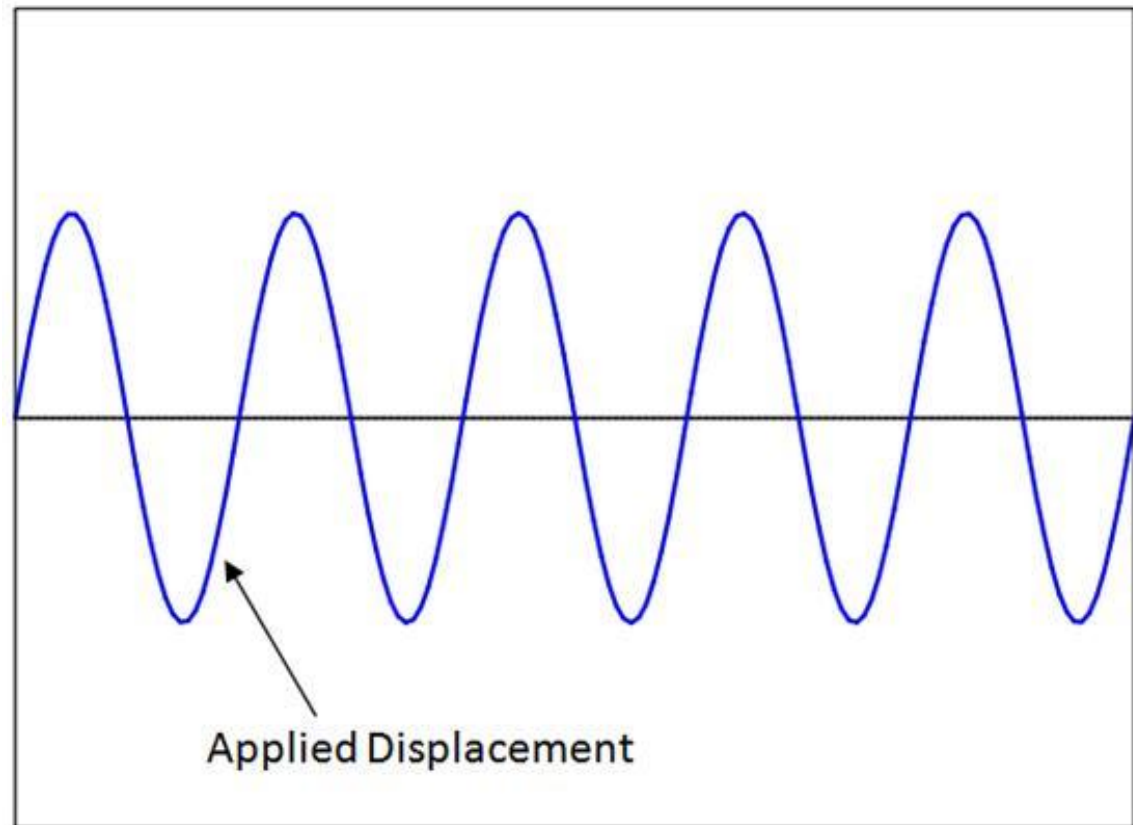
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Dual cantilever  
bending

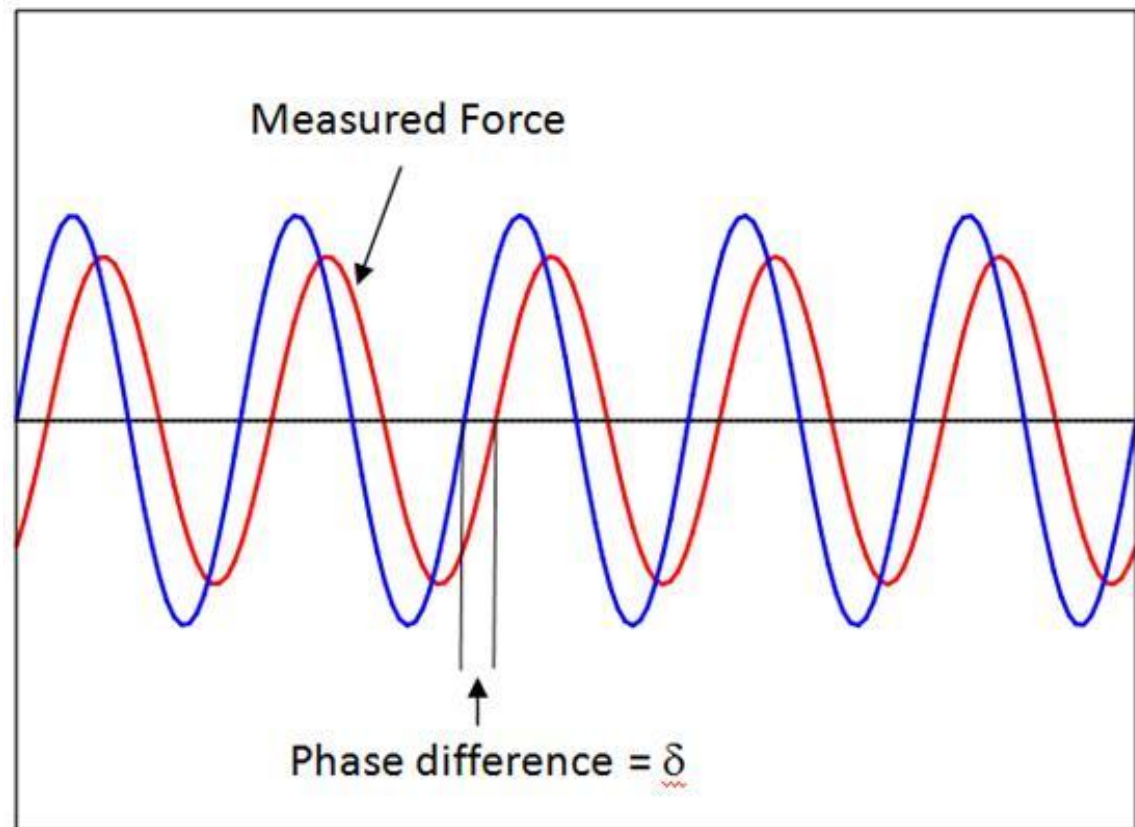
# Viscoelastic Behaviour and the Glass Transition

- For viscoelastic materials, force and displacement are not in phase



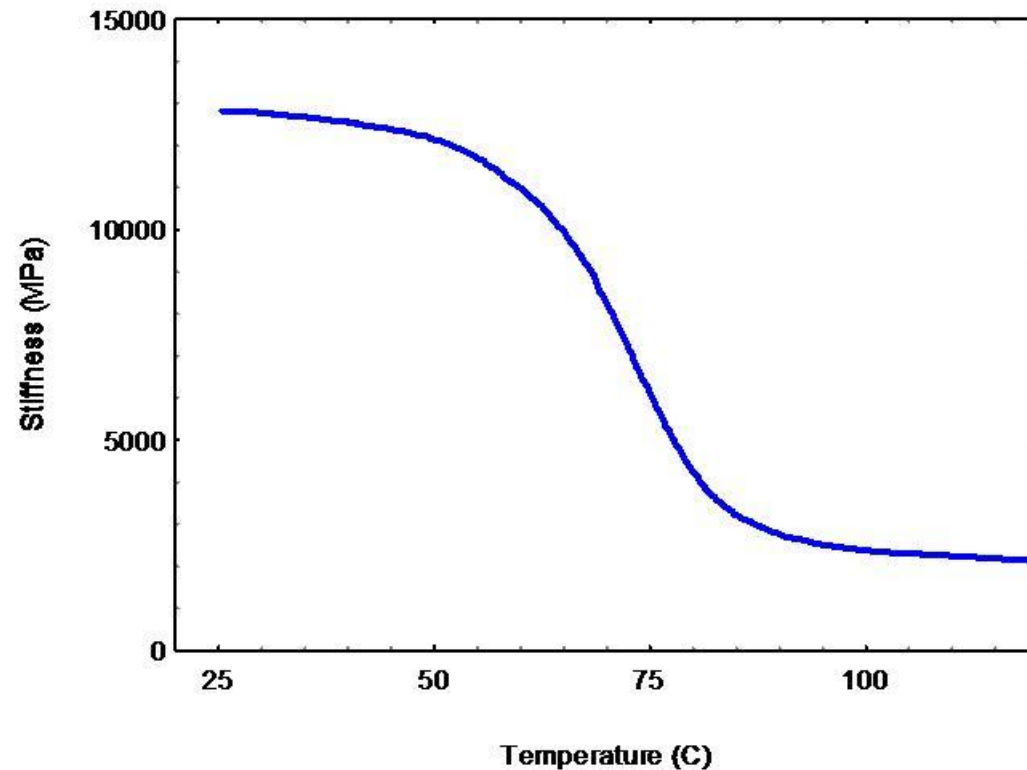
# Viscoelastic Behaviour and the Glass Transition

- Phase difference ( $\tan \delta$ ) is a measure of the damping, hysteresis, energy loss



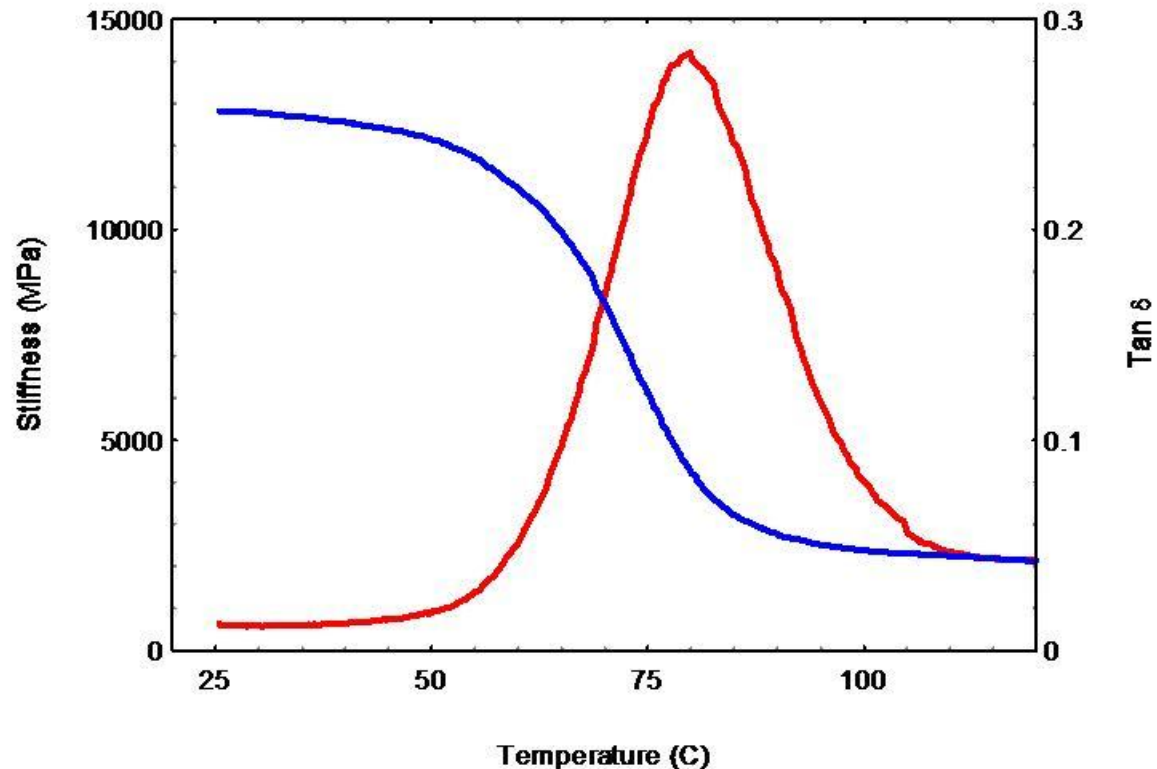
# Viscoelastic Behaviour and the Glass Transition

- Stiffness drops dramatically around  $T_g$



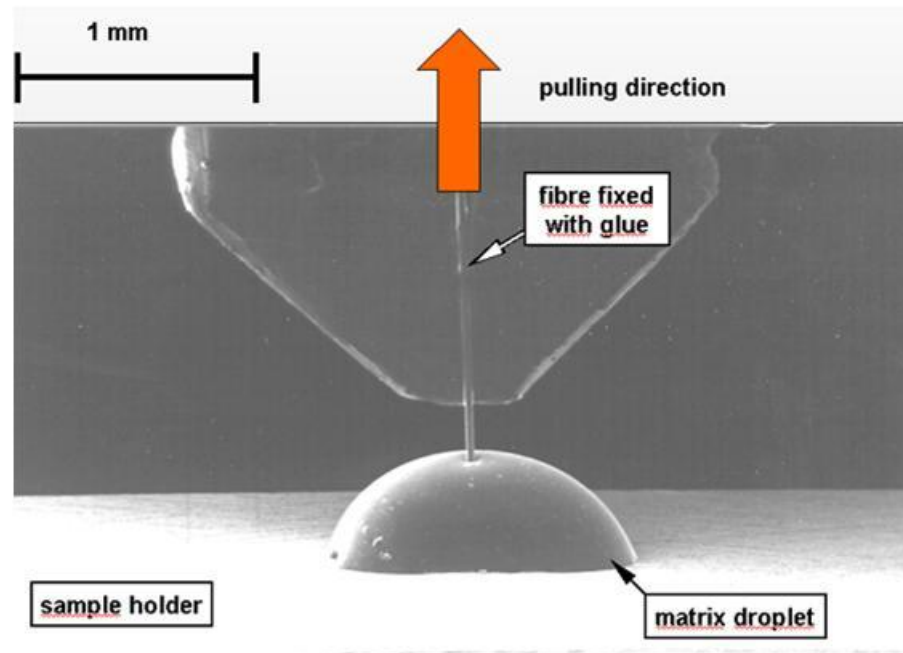
# Viscoelastic Behaviour and the Glass Transition

- Damping reaches a peak at  $T_g$
- For most thermoset composites,  $T_g$  represents upper use limit



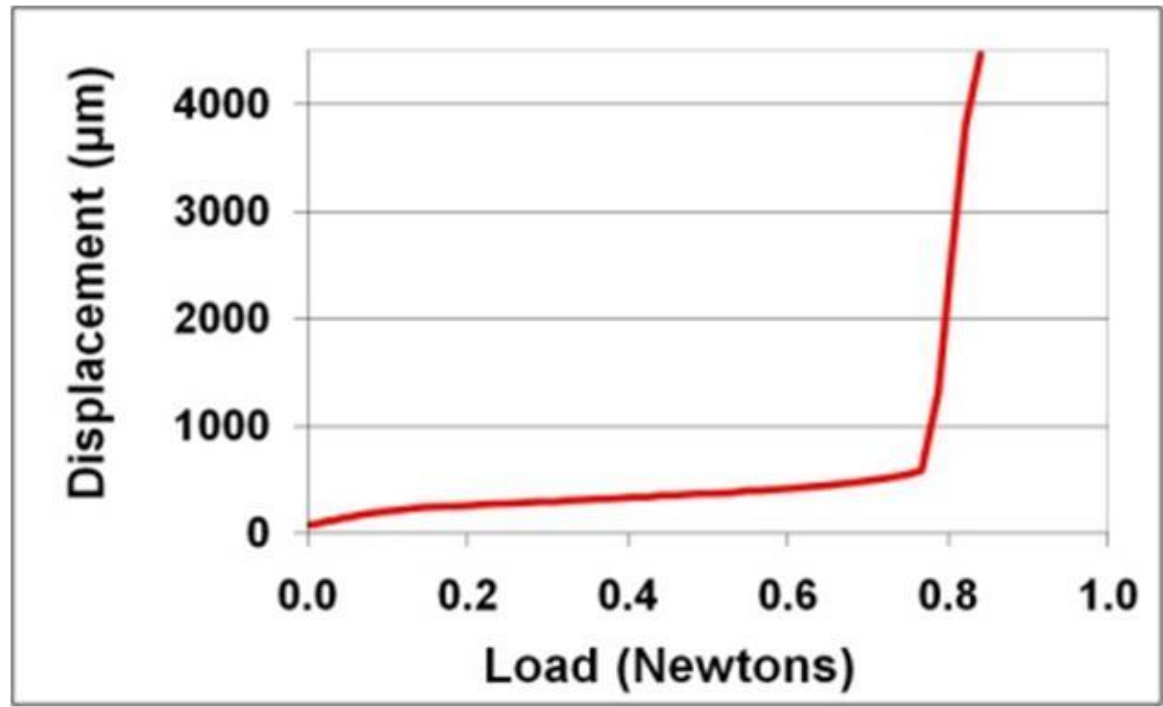
# Interfacial Bond Strength

- DMTA can be used to measure fibre pull-out strength
- Individual fibre mounted, DMTA lowers fibre into resin
- After curing, tensile mode used to measure bond strength



# Interfacial Bond Strength

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- Individual fibre mounted, DMTA lowers fibre into resin
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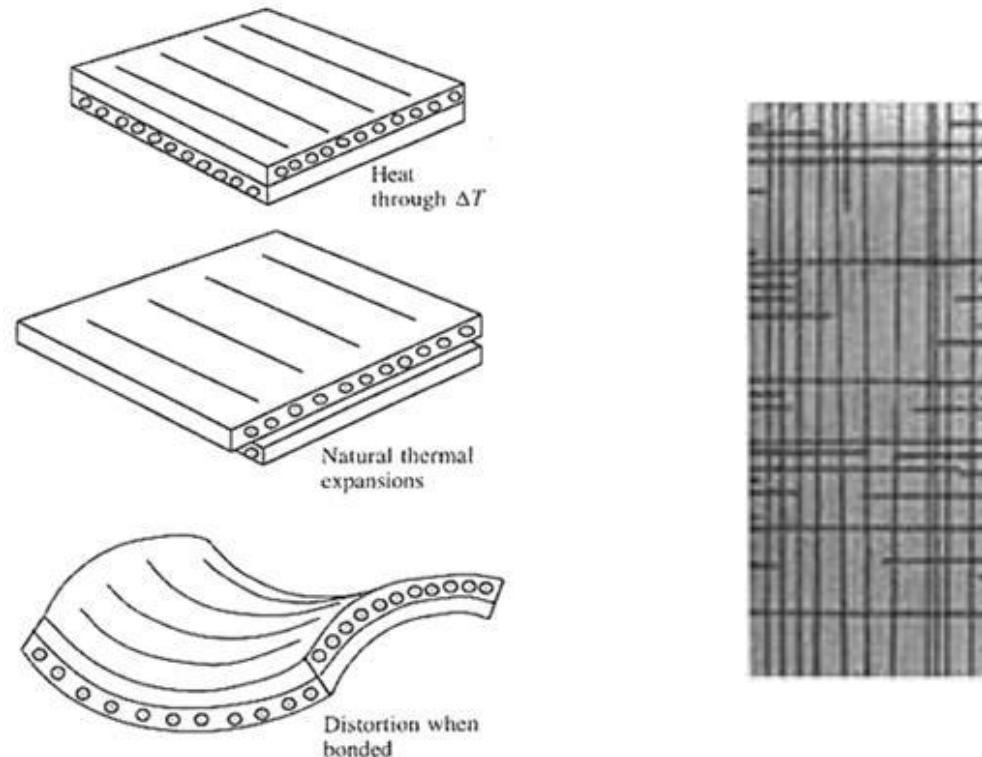
# Thermal Expansion

- Thermal expansion with composites is an important issue.
- Carbon, aramid and polymer fibres have lower thermal expansion along their length than most other materials.

MATERIAL	DIRECTION	THERMAL EXPANSION
Aluminium alloy	N/A	$23 \times 10^{-6} \text{ K}^{-1}$
Carbon fibre	Along fibre	$2 \times 10^{-6} \text{ K}^{-1}$
UD Carbon / epoxy	Along fibres	$3 \times 10^{-6} \text{ K}^{-1}$
UD Carbon / epoxy	Across fibres	$40 \times 10^{-6} \text{ K}^{-1}$

# Thermal Expansion

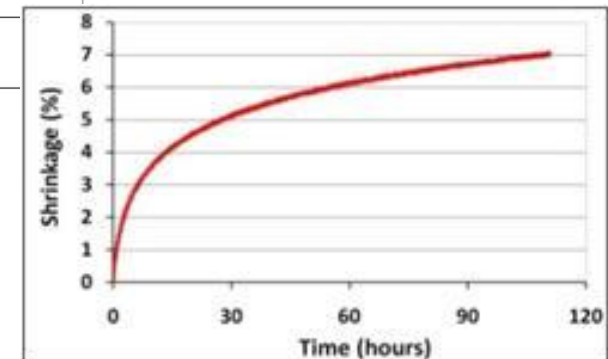
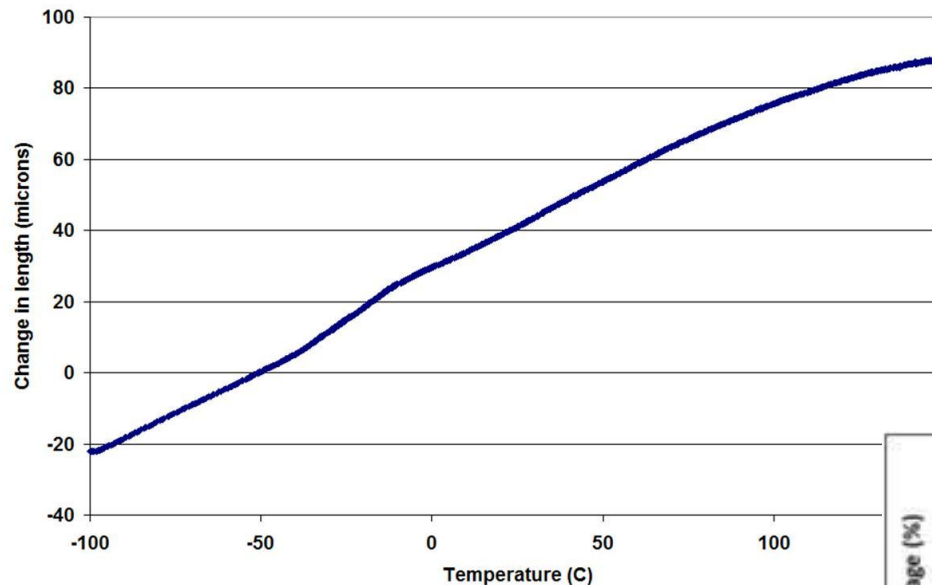
- The difference in thermal expansion can lead to significant thermal stresses
  - In 0/90 laminates
  - When bonded to other materials



X-ray image  
of thermal  
fatigue  
cracks in  
0/90  
composite

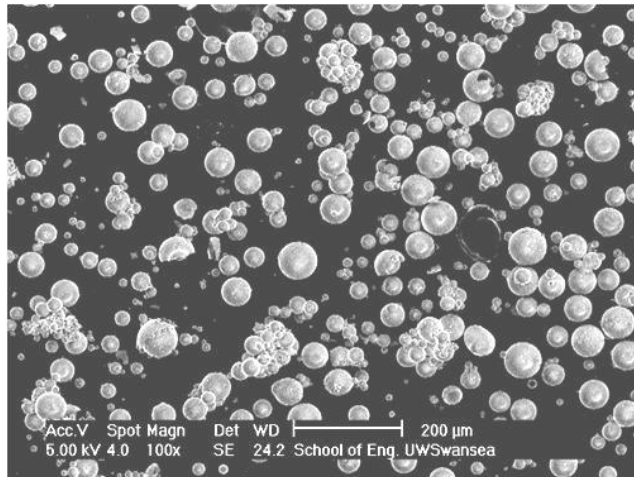
# Thermal Expansion & Orientation Recovery

- By operating in TMA mode, DMTA can measure sample length as temperature changes
- Can measure thermal expansion and recovery of orientation



# Thermal Conductivity

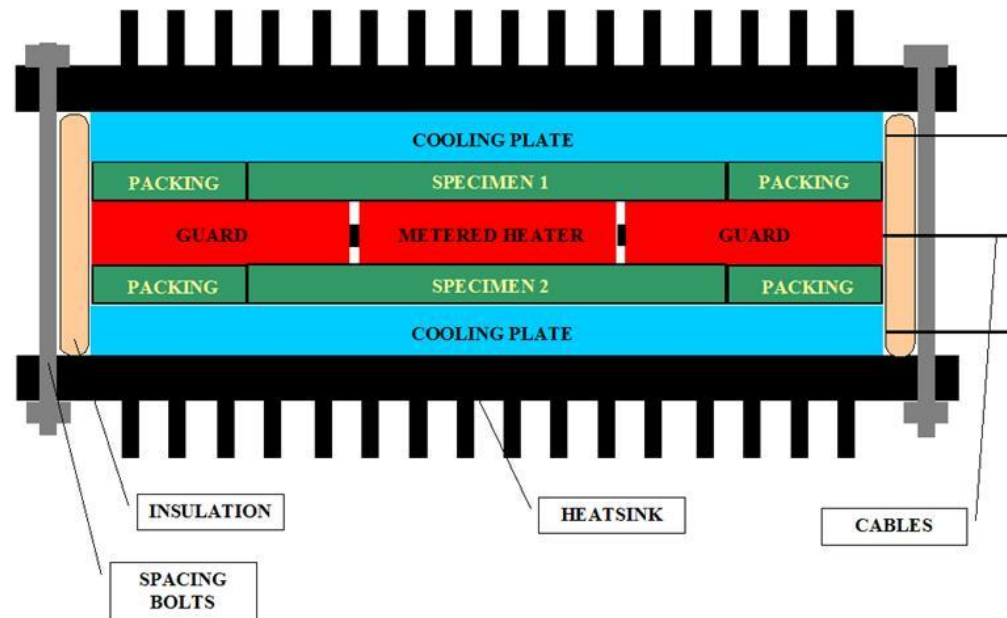
- K value – inherent material property –  $W/mK$   
Heat flow through unit area of unit thickness per degree temperature difference.
- U value – specific to thickness used –  $W/m^2K$   
Heat flow through unit area of the measured product per degree temperature difference.  
Widely used in construction sector for panels of several constituent materials.



Hollow glass spheres used in syntactic foam insulation layer for sub-sea oil pipes

# Thermal Conductivity

- Can use transient methods
- Steady heat flow methods are more accurate
- Guarded hot-plate method



# Thermal Conductivity

## Heat Flux Method: Fox 50-110

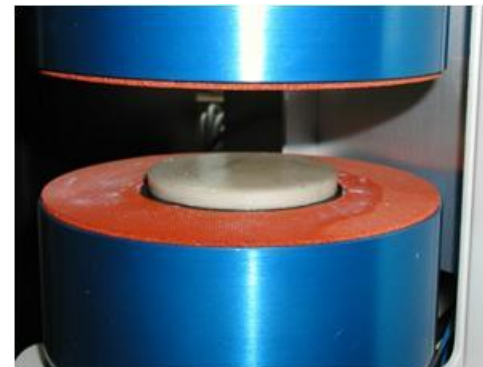
Temperatures from  $-10^{\circ}\text{C}$  to  $110^{\circ}\text{C}$

Measurement range from  $0.02 \text{ W/mK}$  to  $10 \text{ W/mK}$



Good interface contact is vital

Flat and smooth samples  
Thermal grease or silicone oil at surface



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Thank you for listening.

Any questions?

